Van der Waals Equation
Devation from ideal gas laws

Notes prepared by

Prof Dr Hikmat S. Al-Salim

The compression factor *Z*

- The **compression factor**, Z, of a gas is the ratio of its measured molar volume, $V_m = V/n$, to the molar volume of a perfect gas, V_m^o, at the same pressure and temperature:

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$$Z = \frac{V_m}{V_m^o}$$

- Because the molar volume of a perfect gas is equal to RT/p, an equivalent expressi

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$$pV_m = RTZ$$

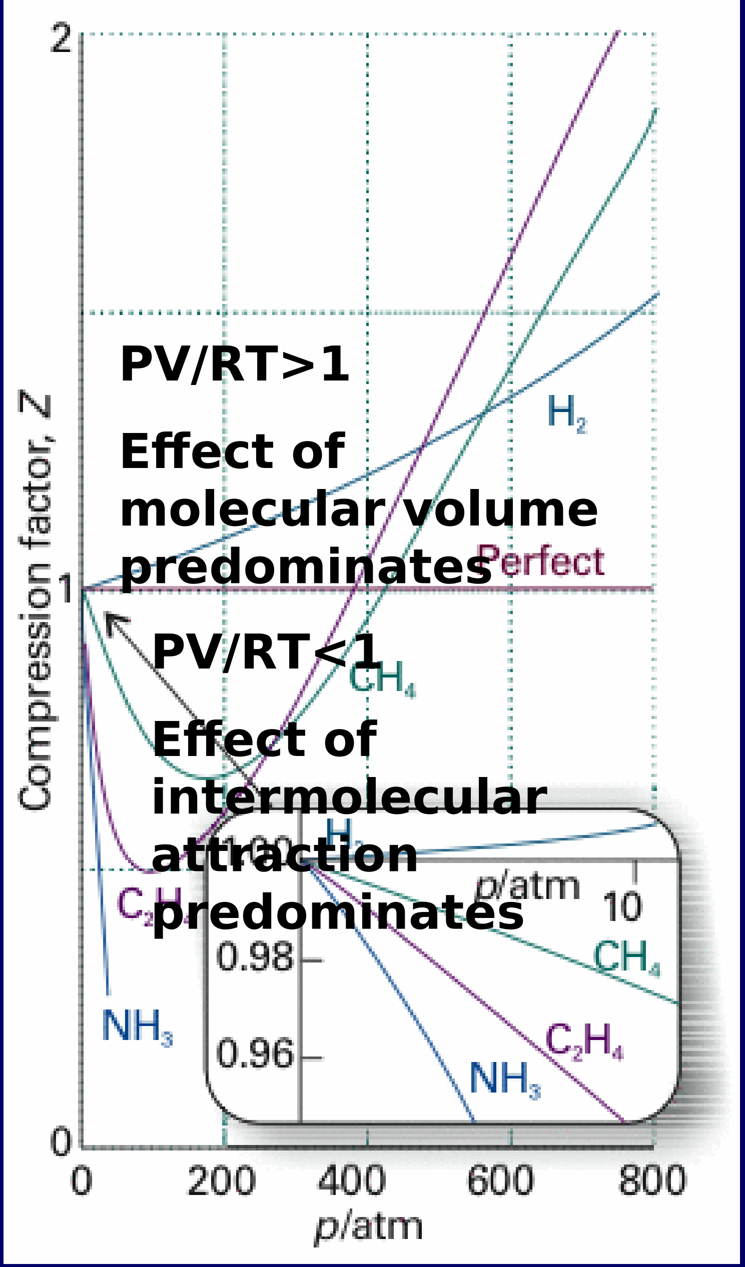
$$Z = \frac{RT}{\rho V_m^o}$$

- Because for a perfect gas $Z = 1$ under all conditions, deviation of Z from 1 is a ***measure*** of departure from perfect behaviour.

$$pV = nRT$$

EXPERIMENTALLY

A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes. At high pressures, all the gases have $Z > 1$, signifying that they have a larger molar volume than a perfect gas. Repulsive forces are now dominant. At intermediate pressures, most gases have $Z < 1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.



PV/RT>1

Effect of molecular volume predominates

PV/RT<1

Effect of intermolecular attraction predominates

- The behavior of real gases usually agrees with the predictions of the ideal gas equation to within (±) 5% at normal temperatures and pressures. At low temperatures or high pressures, real gases deviate significantly from ideal gas behavior.
- van der Waals developed an explanation for these deviations and an equation that was able to fit the behavior of real gases over a much wider range of pressures.

The kinetic theory assumes that:

1. gas particles occupy a negligible fraction of the total volume of the gas.
2. the force of attraction between gas molecules is zero.

At normal pressures, the volume occupied by gas molecules is a negligibly small fraction of the total volume of the gas. But at high pressures, this is no longer true. As a result, real gases are not as compressible at high pressures as an ideal gas. The volume of a real gas is therefore larger than expected from the ideal gas equation at high pressures.

- Van der Waals proposed that we correct for the fact that the volume of a real gas is too large at high pressures by ***subtracting*** a term *(b)* from the volume of the real gas before we substitute it into the ideal gas equation.
- *(b)* equal to the volume actually occupied by a mole of gas. Because the volume of the gas particles depends on the number of moles of gas in the container, the term that is subtracted from the real volume of the gas is equal to the number of moles of gas times *b*.

$$P(V - nb) = nRT$$

- The assumption that there is no force of attraction between gas particles cannot be true. If it was, gases would ***never*** condense to form liquids. In reality, there is a small force of attraction between gas molecules that tends to hold the molecules together. This force of attraction has ***two*** consequences:
  - gases condense to form liquids at low temperatures .
  - the pressure of a real gas is sometimes smaller than expected for an ideal gas.

- To correct for the fact that the pressure of a real gas is smaller than expected from the ideal gas equation, van der Waals ***added*** a term to the pressure in this equation. This term contained a second constant (*a*) and has the form: an^2/V^2. The complete **van der Waals equation** is therefore written as follows

$$[P + \frac{an^2}{V^2}](V - nb) = nRT$$

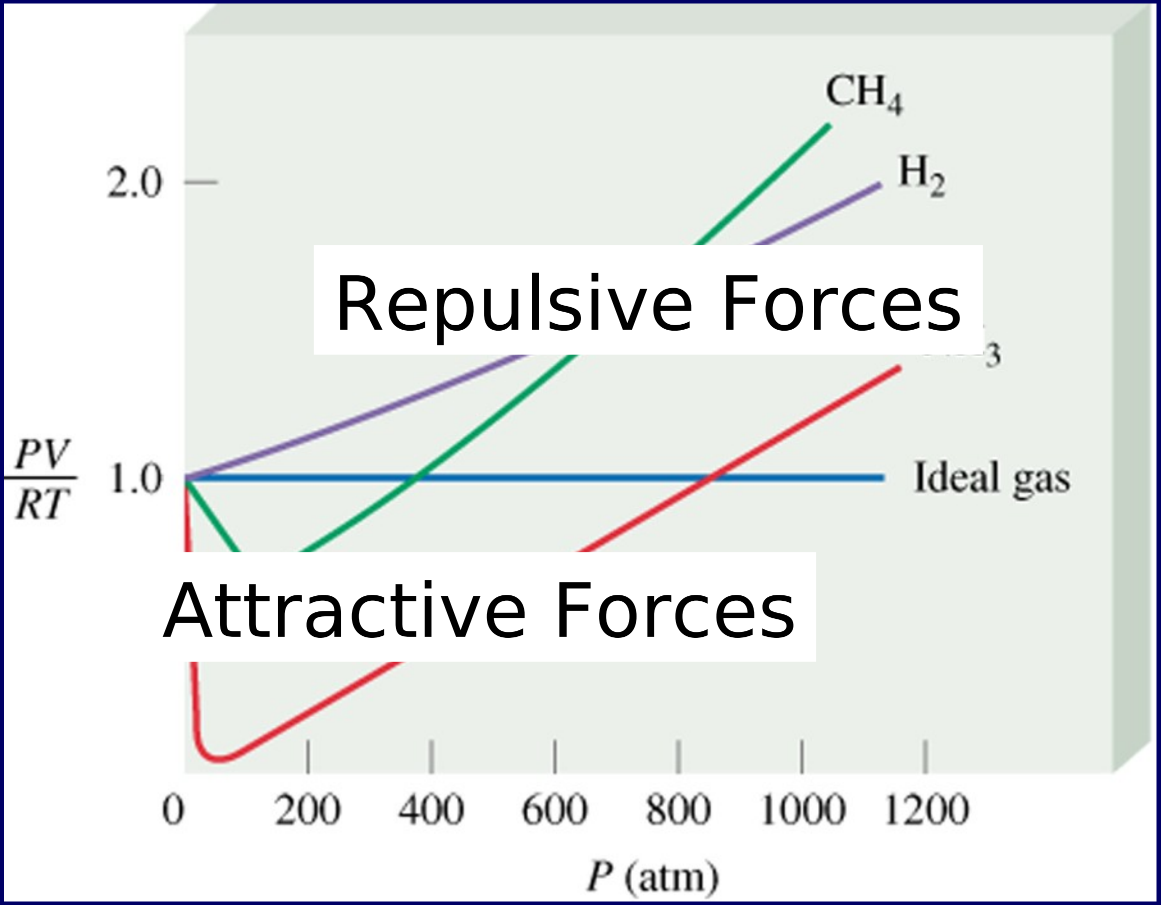
Deviations from Ideal Behavior

1 mole of ideal gas

$$PV = nRT$$

$$n = \frac{PV}{RT} = 1.0$$

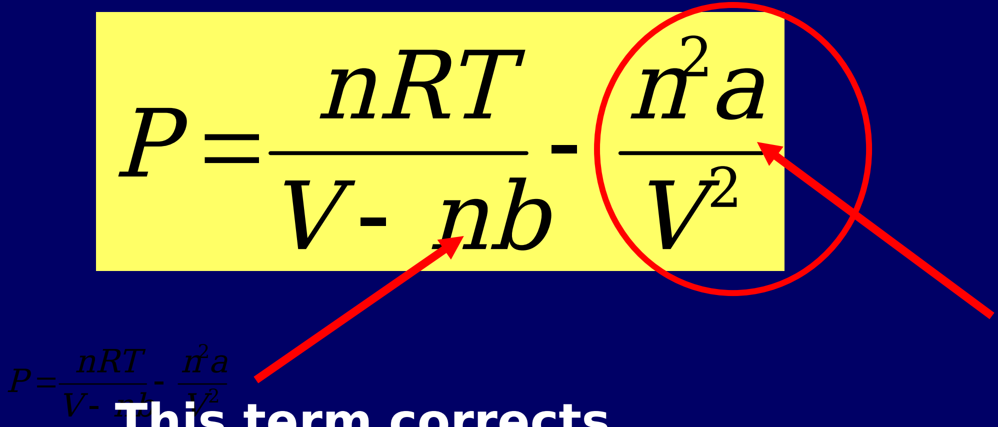
If gases are ideal, then a straight line is obtained


Repulsive Forces

Attractive Forces

The van der Waals Equation

Deviation from ideal gases



$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

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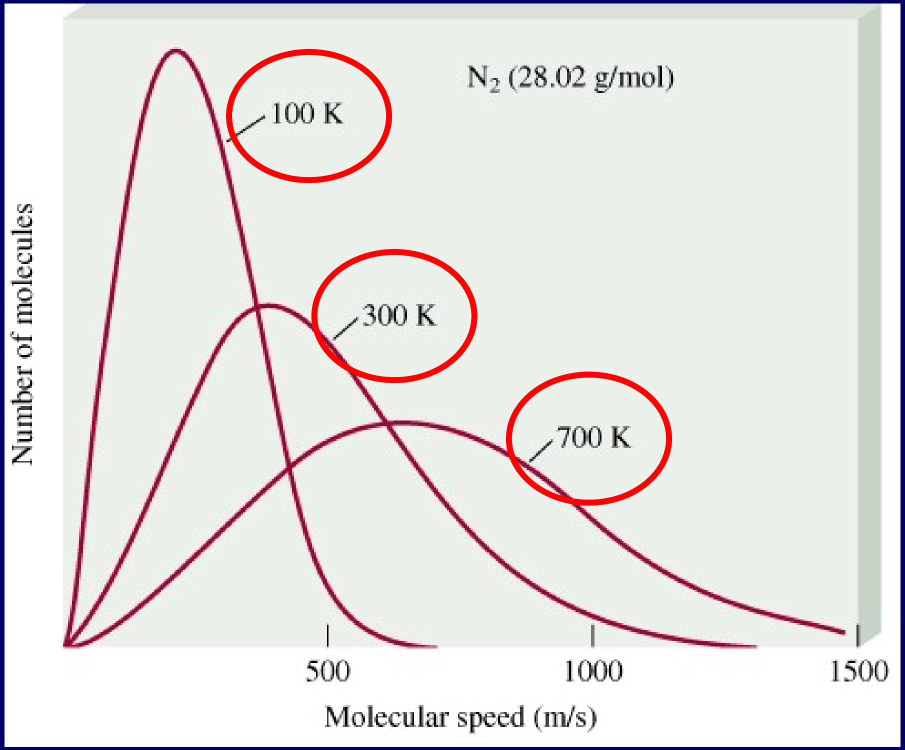
This term corrects for molecular volume

This term corrects for molecular attraction

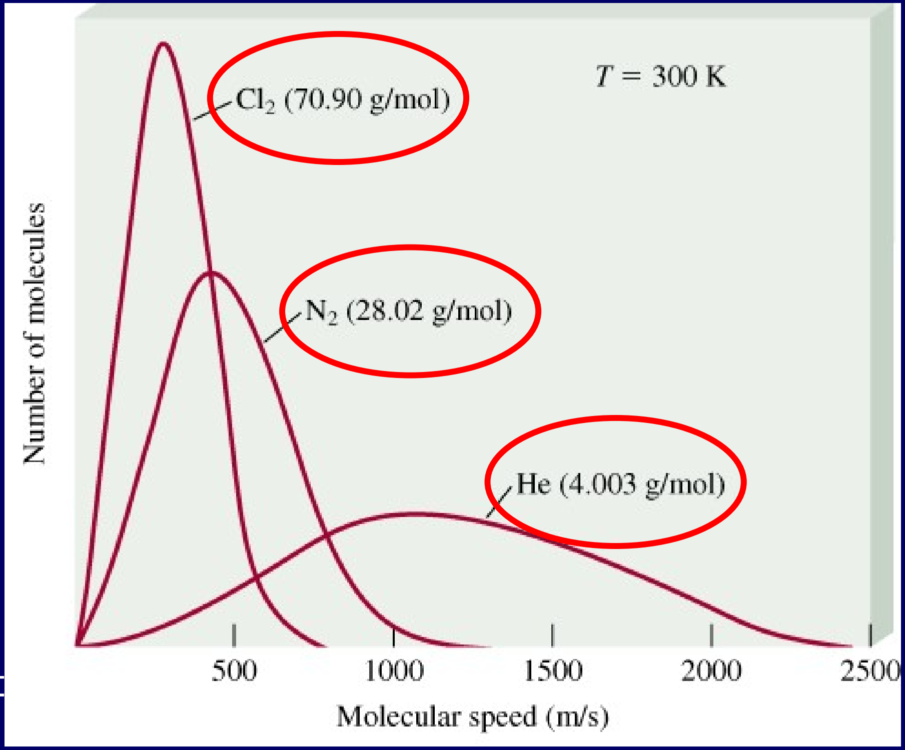
$$\left(P + \frac{n^2 a}{V^2} \right)(V - ab) = nRT$$

This is the general form of Van der Waals Equation



The distribution of speeds
for nitrogen gas molecules
t three different temperatures

The distribution of speeds
of three different gases
at the same temperature



$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

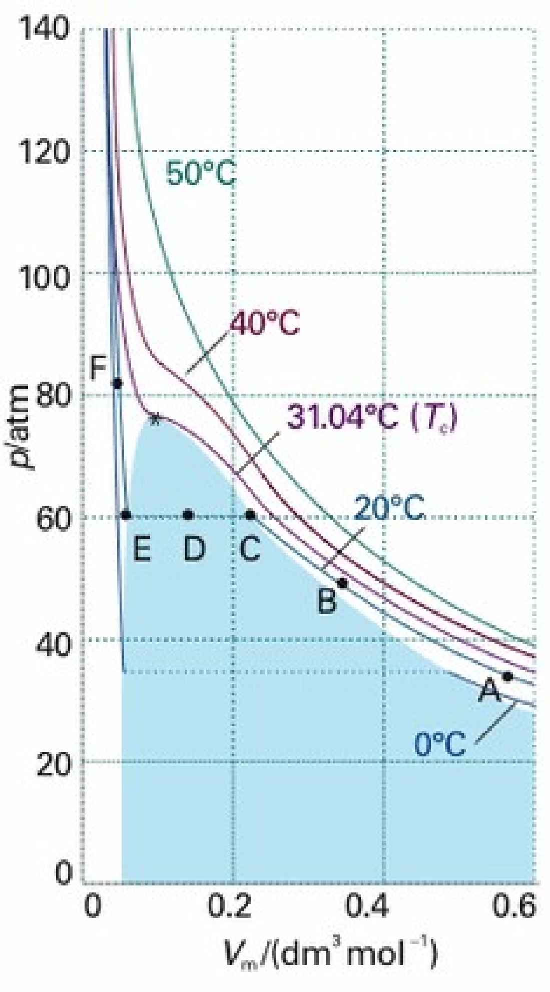
van der Waals Constants for Various Gases

Compound	*a* (L^2-atm/mol^2)	*b* (L/mol)
He	0.03412	0.02370
Ne	0.2107	0.01709
H_2	0.2444	0.02661
Ar	1.345	0.03219
O_2	1.360	0.03803
N_2	1.390	0.03913
CO	1.485	0.03985
CH_4	2.253	0.04278
CO_2	3.592	0.04267
NH_3	4.170	0.03707

Virial coefficients

- Adjacent figure shows the experimental isotherms for carbon dioxide. At large molar volumes and high temperatures the real-gas isotherms do not differ greatly from perfect-gas isotherms. The small differences suggest that the perfect gas law is in fact the ***first term*** in an expression of the form :

$$pV_m = RT(1 + B'p + C'p^2 + \cdots)$$



- A more convenient expansion for many applicat

$$pV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots\right)$$

These two expressions are two versions of the **virial equation of state**

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- By comparing these two expression with the following equat $pV_m = RTZ$ we see that the term in parentheses can be identified with the compression factor, *Z*. i.e

$$pV_m = RT\boxed{\left(1+\frac{B}{V_m}+\frac{C}{V_m^2}+\cdots\right)} \quad = Z$$

The coefficients *B*, *C*,..., which depend on the temperature, are the **second, third**,...**virial coefficients** , the first virial coefficient is 1. The third virial coefficient, *C*, is usually less important than the second coefficient, *B*.

Gas Density & Molar Mass

- The ideal gas equation PV = nRT can be rearranged to give an expression:

$$\frac{n}{V} = \frac{P}{RT}$$

Mass per unit volume

Notice that $\frac{n}{V}$ has the units of moles per liter. Suppose we multiply both sides of the equation by **M** (molar mass) i.e. the number of grams in 1 mole of a substance.

$\frac{nM}{V} = \frac{PM}{RT}$ Note here the product of
$\frac{nM}{V} = \text{the density in g/L}$

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$$\frac{nM}{V} = \text{the density in g/L}$$

$$\frac{\text{Moles}}{\text{Liter}} \times \frac{grams}{mole} = \frac{grames}{Liter}$$

$d = \frac{PM}{RT}$ *this equation tells us that the density of a gas is*

a function of its pressure, molar mass, and temperature

Exercise

- What is the density of carbon tetrachloride vapor at 714 torr and 125 ^{o}C ?
- The molar mass of

$$d = \frac{(714\,torr)(1\,atm/760\,torr)(154\,g/mol)}{0.0821\,L\,atm/mol\,K}$$

$$d = 4.43\,g/L$$

Molar Mass

- The density equation can be written in the following form:
- This equation enables us to measure molar mass from measurement of density of the gas.

$$M = \frac{dRT}{P}$$

Exercise

- A series of measurements are made in order to determine the molar mass of an unknown gas.
- First a large flask is evacuated and found to weigh 134.567 g. It is then filled with the gas to a pressure of 735 torr at 35oC and reweighed. The mass is now137.456 g. Finally the flask is filled with water at 31oC and found to weigh 1067.9 g.(the density of water at 31oC is 0.9997g/L. Assuming the gas equation applies, calculate the molar mass of the gas.

Molar mass of volatile compounds calculations

- An organic colorless liquid was isolated from a petroleum sample. Applying Dumas method, the following results were obtained:
- Volume of the flask=213 ml
- Mass of the flask filled with gas = 78.416 g
- Mass of flask alone =77.834 g
- T at which the flask was filled with the volatile compound = 100.00°C
- Calculate the molar mass of the liquid.

(see solution on next slide)

$$m = 78.416 - 77.834 = 0.582\,g$$

$$P_{atmospheric} = \frac{754}{760} = 0.992\,atm$$

$$change\ volume\ to\ L = \frac{213}{1000} = 0.213\,L$$

$$T = 273.15 + 199 = 373.15\,K$$

$$M_{molar\ mass} = \frac{nRT}{PV} = \frac{0.582\ x\ 0.0821\ x\ 373.2}{0.992\ x\ 0.213} = 84.4\,g/mo$$

Example 1: A steel tank has a volume of 438 L and is filed with 0.885 kg of O_2. Calculate the pressure of O_2 at 24°C.

$$T = 21 + 273 = 294$$

$$n = \frac{0.885\,kg}{32\,g} = 27.7\ mole$$

$$P = \frac{nRT}{V} = \frac{27.7 x 0.0821 x 294}{438} = 1{,}53\,atm$$

- Example : Find the density (in g/L of CO_2 and the number of molecules per liter:
  - (a) at 0°C and 1 atm
  - (b) at room temperature of 20°C and 1 atm.

$$\text{part (a) } d = \frac{M\,x\,P}{RT} = \frac{44.01 x 1}{0.0821 x 273} = 1.96\, g/L$$

now convert from mass per L to molecules/L

$$\frac{1.96}{44.01} x 6.022 x 10^{23} = 2.68 x 10^{23}$$

$$\text{part (b) d} = \frac{M\,x\,P}{RT} = \frac{44.01 x 1}{0.0821 x 293} = 1.83\, g/L$$

$$converting\ from\ mass/L\ to\ molecules/L$$

$$molecules\ per\ L = \frac{1.81}{44.01} x 6.022 x 10^{23} = 2.50 x 10^{23}\ molecules\ per\ L$$